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The Importance of Appropriate Laboratory Procedures for the Determination of Scale Inhibitor Performance

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Abstract

Inhibitor performance in terms of the minimum inhibitor concentration (MIC) or the threshold concentration required to prevent scale is the most important aspect for scale control additives. The laboratory test protocols adopted throughout the industry are very similar and are based upon static "bulk" inhibition performance tests and dynamic "tube blocking" inhibitor performance tests. However it has become evident from field selection studies that performance results, obtained from different laboratories using similar techniques, can be significantly different.

In this paper the various procedural differences are described. Results are presented from an extensive series of comparative performance tests examining both static and dynamic performance against calcium carbonate and barium sulphate scale. The results clearly demonstrate how relatively small differences in test procedure, as currently adopted by different laboratories, can have a significant impact on determined MIC values and comparative performance of different species. Such procedural modifications can therefore impact upon the reliability of data obtained in field chemical selection studies and the determination of dose levels, leading to the selection of less effective products. Tests examine the comparative impact of test procedures on generically different inhibitor species including phosphonate, polyacrylate and polyvinylsulphonate chemistries. The impact of the following aspects are covered:

- The inclusion of bicarbonate ions on both static and dynamic barium sulphate performance tests.
- The manner in which pH adjustment impacts dynamic sulphate and carbonate performance tests.
- Effect of flow rate, un time, coil dimensions and pre-scaling on dynamic barium sulphate and carbonate performance tests.

Significant changes in both MIC values and also product ranking are recorded using variations on the standard test protocols commonly used in different laboratories, which demonstrates that more standardised and field appropriate procedures are required. The results in terms of changes in MIC and ranking of the different products are then explained mechanistically based upon the properties of the different products and the impact of modifications to test procedures. Examples of comparative performance for particular field cases are shown which demonstrate the importance of a field appropriate procedure. Finally, recommended test protocols will be detailed based upon the findings of this study.

Introduction

Inhibitor performance in terms of the minimum inhibitor concentration (MIC) or the threshold concentration required to prevent scale is one of the most important aspects for scale control additives, equalled only by the challenge of effective placement and deployment in today's ever more complex production environments. The laboratory test protocols adopted throughout the industry are very similar and are based upon static "bulk" inhibition performance tests and dynamic "tube blocking" inhibitor performance tests. The conventional static "bulk" or "jar" test procedures commonly adopted are related to that described in the NACE standard TM 0197-97.¹ Such tests have been described in many previous papers for both examination of the factors controlling inhibitor performance^{2,3} and for selecting scale inhibitor products prior to field applications.⁴⁻⁷ These tests are used routinely throughout the industry for scale inhibitor selection and optimisation studies.

In addition to static "jar" tests, dynamic "tube blocking" performance tests are also routinely used for scale inhibitor selection in oilfield environments.^{2,3,5-10} However, these tests often give rise to different selection and ranking of scale inhibitor products than that obtained through conventional "jar" tests. Such discrepancies have been explained in terms of: (i) short residence time (generally < 10 seconds) compared with "jar" tests (2 - 24 hours), (ii) dispersant / anti-agglomerant properties of certain inhibitor species, (iii) differences between nucleation and crystal growth inhibition effects, in addition to (iv) the impact of scale adhesion on the walls of the micro-bore tubing.^{2,3}

There are a number of benefits associated with dynamic performance tests, which have been described in a number of previous publications^{2,3,5,6,8,9,10} as follows:

- Dynamic system, as in oilfield production
- Examines growth and blockage of microbore metal coils
- System under pressure. This allows for routine testing under;
 - higher temperature conditions (> 100°C)^{2,3,6,9},
 - in the presence of bicarbonate ions without loss of pH control^{2,3,5,8}
- Examination of systems in presence of dissolved iron is more readily achievable, provided feed brines are adjusted accordingly to prevent oxidation of Fe(II) → Fe(III)¹⁰

The main disadvantage of dynamic performance tests relates to extremely short residence time, generally of order < 10 seconds. Although this may be appropriate for certain applications such as boiler systems, it is not appropriate to the long residence time (often of the order of hours) in which oilfield scale inhibitors may be expected to perform. This may mean that dispersants, anti-agglomerants, or nucleation inhibitors would be favoured.^{2,3} Care must therefore be taken when interpreting results and it is often recommended that both longer (more field specific) residence time static "jar" tests (in which field temperature and pressure and, potentially pH and bicarbonate content may be compromised) and dynamic "tube blocking" tests (in which residence times may be compromised) should be conducted where possible. The results can be interpreted appropriately taking into account the difference in predominant modes of interaction by different products.^{2,3,9}

Finally, although the conventional dynamic "tube blocking" test probes (at least in part) the ability of scale inhibitors to prevent adherence and growth within micro-bore coils,^{2,3,8} the relationship between bulk homogeneous nucleation and growth and heterogeneous nucleation and growth at metal surfaces (adhesion) is not well defined. This relationship is currently the subject of much ongoing research as it is recognised that heterogeneous growth at metal surfaces (scale adhesion) can be a much more serious problem to tackle than bulk precipitation.¹¹⁻¹⁹ For homogeneous (bulk) precipitation, suspended particles may remain in the bulk fluid and be transported to surface facilities rather than causing blockages to the flow lines.

Outline of Current Study

As discussed above, the laboratory test protocols adopted throughout the industry are very similar and are based upon static "bulk" inhibitor performance tests and dynamic "tube blocking" inhibitor performance tests. However it has become evident from field selection studies that performance results obtained from different laboratories using similar techniques can be significantly different.

In this paper, the various procedural differences are described. Results are presented from an extensive series of comparative performance tests examining both static and dynamic performance against calcium carbonate and barium sulphate scale. The results clearly demonstrate how relatively small differences in test procedure, as currently adopted by different laboratories, can have a significant impact on determined MIC values and comparative performance of different species. Such procedural modifications can therefore impact upon the reliability of data obtained in field chemical selection studies and the determination of dose levels, leading to the selection of less effective products. Tests examine the comparative impact of test procedures on generically different inhibitor species including phosphonate, polyacrylate and vinylsulphonate chemistries. The impact of the following aspects are covered:

- The inclusion of bicarbonate ions on both static and dynamic barium sulphate performance tests.
- The manner in which pH adjustment impacts dynamic sulphate and carbonate performance tests.
- Effect of flow rate, run time, coil dimensions and pre-scaling on dynamic barium sulphate and carbonate performance tests.

In summary, significant changes in both MIC values and also product ranking are recorded using variations on the standard test protocols which are commonly used in different laboratories and this demonstrates that more standardised and field appropriate procedures are required. The results in terms of changes in MIC and ranking of the different products are then explained mechanistically based upon the properties of the different products and the impact of modifications to test procedures. Examples of comparative performance for particular field cases are shown which demonstrate the importance of a field appropriate procedure. Finally, recommended test protocols will be detailed based upon the findings of this study.

This results presented in this paper are discussed in the following areas:

Series (I): Mungo Specific Studies. This examines the impact of test methodology on ranking of scale inhibitor products and the determination of field MIC values in a moderate / severe barium sulphate scaling environment.

Series (II): Examination of Factors Impacting Recorded Performance. This series of tests examines the effects of procedural changes in more detail, in particular (i) small changes in test pH and (ii) the inclusion of bicarbonate ions; on the determined MIC values for two generically different

commercial products in a moderate / severe barium sulphate scaling environment (Mungo conditions as in series (I)).

Series (III) Low Sulphate and Carbonate Scaling Brine Systems. This series of experiments examines the impact of different procedural factors on the performance (MIC values) and ranking for three generically different scale inhibitor species including phosphonate (DETPMP), polyacrylate (PPCA) and polyvinylsulphonate (PVS) based inhibitors. The various brine compositions used throughout this study are presented in Table 1. The chemical structures of the "generic" scale inhibitors species used in experimental series (III) are presented in Figure 1.

Series (I): Mungo Specific Studies

Initial Product Selection Tests. Results from a chemical selection study conducted under Mungo test conditions are presented in a related paper presented at this conference.⁷ However, when comparing the results recorded in the test laboratory with those recorded during pre-selection by the suppliers, it was evident that quite different performances were recorded. In addition, initial comparative tests under field specified conditions illustrated significant differences both in the determined minimum inhibitor concentrations (MIC's) and more importantly the product ranking, when product ranking was conducted under static "jar" and dynamic "tube blocking" conditions. The work presented in this paper therefore examines the impact of small changes in test procedure on inhibitor performance and product ranking when tested under both static and dynamic conditions. In initial tests, three commercial scale inhibitor products were examined which represented a polymeric based inhibitor (Pol) and two phosphonate-based inhibitors (Phos1 and Phos2). Later tests were conducted without the inclusion of Phos2.

Initial Product Selection Test Results. Initial static barium sulphate inhibitor performance tests were conducted using a 50:50 mix of Mungo FW/SW at pH 6.0 in the absence of bicarbonate.⁷ The following ranking of scale inhibitor performance was obtained under these conditions:

	Polymer	>	Phos 1 ~ Phos 2
MIC*	10 - 15 ppm		~ 20 ppm

Dynamic carbonate performance tests were carried out under similar conditions (50:50 Mungo FW/SW, pH 6.0, [bicarbonate] = 250 ppm, flow rate Q = 6 ml/min, System pressure = 1,000psi), giving the following results, as indicated in Figure 2:

	Polymer	>	Phos 2	>	Phos 1
MIC*	25 ppm		35 ppm		50 ppm

In addition, due to the recorded poor performance of the products when compared with the static performance tests, the pass criteria were reduced to < 1 psi increase in DP over 100 minutes of run time as opposed to the initial specification of < 1 psi increase in DP over 240 minutes (4 hours) of run time.

Thus, not only were different MIC's recorded by the different tests procedures, but the ranking of the products was also altered. To better understand the effect of the test conditions on such performance tests, a more in depth investigation was undertaken.

Following rationalisation of the test protocols as described in this paper, further dynamic "tube blocking" tests were conducted which compared the performance of the polymer product (Pol) and one of the phosphonate products (Phos 1). These tests were conducted in the absence of bicarbonate ions under the following conditions; 50:50 Mungo FW/SW, pH 6.0, [bicarbonate] = 0 ppm, flow rate Q = 6 ml/min, System pressure = 250 psi). In addition the pass criteria were changed back to the original specification of < 1 psi increase in DP over 240 minutes (4 hours) of run time. The final MIC values recorded were as follows (Figure 3):

	Polymer	>	Phos 1
MIC*	5 - 10 ppm		15 - 25 ppm

Prior to these tests, the initial field MIC for the polymeric inhibitor (Pol) was set at 25 ppm, being the value recorded in the initial dynamic tube blocking tests and representing a worst case when comparing static and dynamic performance tests. This value was subsequently used to determine the field squeeze lifetime.⁷ However following the work reported in this paper, the field MIC was revised downwards towards 10 - 15 ppm. This value of 10 - 15 ppm is based upon the static performance tests, which itself is higher than the revised dynamic performance tests, and would be expected to result in significantly longer squeeze lifetimes for this product and consequential cost savings. This serves to illustrate the importance of effective product selection and MIC determination in today's complex environments in which well access can be extremely expensive when compared with chemical costs.^{7, 20} Determination of an MIC higher than the optimal figure can lead to expensive and unnecessary early re-treatment whereas determination of an MIC lower than the optimal figure can result in uncontrolled scale formation, subsequent loss of production and well re-entry. In complex subsea reservoirs, in which fluids from several production wells are often commingled at a subsea template and produced along single seabed flowlines, monitoring from individual wells remains an unsolved challenge.^{7, 20} The extremely high costs associated with well access means that it is more important than ever to select appropriate inhibitor dose levels (MIC values) in the laboratory rather than rely upon subsequent optimisation in the field.

Series (II): Examination of Factors Impacting Recorded Performance

Static Barium Sulphate Performance Tests. Static barium sulphate inhibition efficiency tests were conducted to examine the performance of the scale inhibitors under the following test conditions, representing the worst case barium sulphate scaling regime expected during production.

Brine system:	50:50 Mungo FW/SW (see Table 1 for brine compositions)
Test temperature:	95°C
Test pH:	various
Residence times:	2, 4 and 22 hours

The static barium sulphate scale inhibition efficiencies were then compared using previously described techniques.^{1,2,4,7} However, during pre-selection studies it was evident that different suppliers were using procedures which, although based upon previously reported methodologies,^{1,2} contained modifications. Of particular concern was the inclusion or omission of bicarbonate ions in static barium sulphate performance tests. This was of concern since pH control in bulk jar tests would be expected to be difficult in the presence of bicarbonate ions under normal test conditions.^{2,3} Changes in pH are known to have a controlling influence on inhibitor performance, both in terms of inhibition efficiency and also brine compatibility.^{2,3,4,5} In addition, the influence of pH is different for different chemical types and is related to the pKa values of the active functional groups within the inhibitor molecules.^{2,3,6,20-24} To examine this effect, minimum inhibitor concentrations (MIC's) were determined under a range of modified test conditions, the MIC being the minimum concentration of scale inhibitor necessary to provide >80% inhibition efficiency at 4 hr residence time. Six test conditions have been examined to determine the effect of pH and bicarbonate ion concentration on scale inhibitor performance. These test conditions are summarised in Table 2. Note that the pH chosen for tests ci and cii represent respectively the initial and final pH's recorded in test e. Tests were conducted using both the polymer (a vinyl sulphonate/acrylate co-polymer) and the phosphonate product and the determined MIC values for both products are given in Table 3.

Effect of pH on SI Performance. It is clear from the data presented in Table 3a and shown in Figure 4 that pH has only a minimal impact on the scale inhibitor performance of the polymer within the pH range tested. A greater impact is observed for the phosphonate-based product, with increasing pH giving increased performance (Figure 5). This difference in behaviour between the two products is due to their different chemical natures. The polymer product contains sulphonic ($pK_a \ll 2.5$) and carboxylic ($pK_a \sim 4.5$) acid functional groups. The polymeric nature of this product however means that the pKa values of the acrylic acid units will be less discrete but may be expected to range between 3 and 6.* The phosphonate-based product contains phosphonic acid groups as the active functional groups. Although the pKa for a single phosphonic acid group may be in the order of $pK_a \sim 4-5$ the presence of several phosphonic acid groups will again be expected to result in a pKa range. For example, the pKa values for DETPMP as examined in Series (III) range from $pK_{a3} = 2.8$, through $pK_{a7} = 7.2$ to $pK_{a10} = 12.0$.² Effective barium sulphate scale inhibition requires that these acid groups be ionised. At pH 5.5, essentially all of the sulphonic acid

groups in the polymer product are already ionised, and so increasing the test pH has minimal effect. In the case of the phosphonic acid based product however, a significant number of functional groups remain *unionised* (and thus less active) at pH 5.5. Increasing the test pH will therefore increase the amount of ionised (active) phosphonate groups present, and so increase the performance of the phosphonate-based product.

*Note: the pKa range for of the acrylate functional groups in the PPCA inhibitor examined in series (III) results in almost no dissociation at pH 2 and nearly complete dissociation at pH7.

Effect of Bicarbonate on SI Performance. Addition of HCO_3^- had a minimal impact on the performance of the polymer product (Table 3a, Figure 4). With the phosphonate product, addition of bicarbonate leads to an increase in performance (Table 3a, Figure 5). This is most likely due to an increase in solution pH during the test run, although common ion effects may also account for a further marginal increase in performance. The controlling influence of pH and the effect of pH on scale inhibitor performance has been described previously.^{2,20-23} As the susceptibility of a given scale inhibitors performance to pH is governed by the inhibitors pK_a values, it is obvious that different inhibitors *even within the same chemical class* will respond differently to pH changes, potentially altering the relative performance ranking of a set of inhibitors. This may help in explaining the change in ranking recorded for the two phosphonate based product (Phos 1 and Phos2) when tested by static and dynamic performance tests in the "Initial Product Selection Tests" described in Series (I) of this paper. This work therefore reiterates the importance of pH control in static barium sulphate performance tests.² If performance tests are to be conducted at pH conditions expected prior to evolution of CO_2 into a gas phase (as the pressure in the system drops below the CO_2 bubble point), then bicarbonate ions should not be added unless more sophisticated test apparatus is employed so as to ensure that the CO_2 remains in solution and the brine pH remains controlled to that required.²

Other related studies indicate that effective pH control can be obtained in carbonate containing static tests by the use of narrow neck crimp seal vials,³ the procedure appears less routine than conventional static tests in which wide neck bottles are generally used for ease of sampling.

Dynamic Carbonate Scale Performance Tests. The influence of pH, bicarbonate ion concentration and system pressure on scale inhibitor performance has been examined for the two products in a series of tests. These tests were conducted using the following standard conditions:

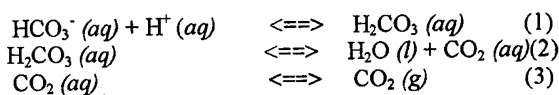
System Pressure:	250 psi
System Temperature:	107°C
Coil dimensions:	ID ~ 0.8 mm
	L => 1,000 mm

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Brine mixture:	50:50 Brine /1: Brine /2 to give 50:50 Mungo FW / SW. (Table 1 for brine composition)
Pass/Fail criterion:	Initial tests 1psi increase in DP over 4 hour.
Flow rates:	6 ml /min combined flow rate (50:50 mix, 3ml/min per brine).
pH Adjustment:	As indicated in Table 3b

In these tests, the M.I.C. was defined as being that level of scale inhibitor necessary to prevent a differential pressure increase of 1 psi over 4 hours. The results obtained are given in Table 3b.

As expected from the results obtained for the static performance tests, lowering the test pH from 6.0 to 2.5 results in a marked decrease in performance for both polymer and phosphonate product. At such a low pH both the carboxylic acid groups of the polymer and phosphonic acid groups of the phosphonate are predominantly in the unionised form, and hence are much less effective as scale inhibitors. Addition of bicarbonate resulted in significantly higher recorded MIC's for both the polymer and phosphonate based products when tested at apparently similar *measured* pH values to those examined in the absence of bicarbonate ions. When the mixed pH was measured at 6.0 with 250 ppm added bicarbonate, the polymer and phosphonate recorded MIC's of >40 ppm and 20 – 40 ppm respectively (*cf.* respective MIC's of 5 – 10 ppm and 2 – 5 ppm in the absence of bicarbonate). Increasing the test pH to >7 (by omitting to adjust the pH of brine 1) gave MIC's of 5 – 10 ppm (polymer) and 2 – 5 ppm (phosphonate), equivalent to those recorded at pH 6.0. This reduction in performance is much greater than would be expected based on the static performance test results. This can be explained if, in the presence of bicarbonate ions, using the standard dynamic test procedure results in much lower mixed brine pH *in situ* than would be predicted by measuring the mixed brine pH at atmospheric pressure. That such a phenomenon occurs can be demonstrated by means of the following simple chemical equilibria (equations 1 – 3);



In the standard dynamic carbonate test procedure, bicarbonate is added to brine 2 and acid is added to brine 1 such that the desired test pH is obtained when brines 1 & 2 are mixed in the appropriate ratio at ambient conditions (20°C, atmospheric pressure) in an open system. Under these conditions, some CO₂ (g) will be evolved from the system allowing equilibrium to be re-established at the desired test pH, i.e. the simple equilibria above allow the system to buffer against small additions of acid. However, during dynamic "tube blocking" tests the two brines are mixed *in situ* in a pressurised system. Under such circumstances, liberation of CO₂ (g) becomes

much less favourable. Consequently, the conversion of HCO₃⁻ to CO₂ proceeds to a much lesser extent than if mixing occurred at atmospheric pressure. Therefore, a greater amount of H⁺ remains in the brine mixed in a closed system under pressure than was the case at atmospheric pressure in an otherwise open system, resulting in a lower *in situ* test pH and hence reduced scale inhibitor performance. From the results obtained, it can be predicted that when the pH of these brines are unadjusted (mixed pH ~7.0 at atmospheric pressure), the actual *in situ* test pH is approximately 6.0.

To examine this further, a generic polyvinylsulphonic acid scale inhibitor (PVS) as used in Series III of this paper was examined at test pH 2.4 and 6.0 in the absence of bicarbonate ions. In each case an MIC of ~1 ppm (*active*) was recorded for this product as also indicated in Table 3b. As described above, the low pKa of the active functional groups with this chemical would mean that the inhibitor would remain effectively dissociated even at pH values as low as 2.4 and minimal reduction in performance would be expected, as was observed.

pH Modelling Studies. To more fully understand the conditions pertaining when the two brines are mixed within a closed system at pressure (as in the dynamic "tube blocking" coil) the theoretical pH's expected following mixing of brines 1 & 2 (see Table 1) to give a mixed brine representing 50:50 Mungo FW/SW were examined. This modelling was performed using ScaleChem v2.2.

No pH adjustment, [Bicarb] = 500 ppm in brine/2 (250 ppm in mixed brine system). The results indicated that, with no evolution of CO₂ from the system, not adjusting the pH of brine/1 results in a calculated mixed pH of 6.7 (at ambient T,P) which is in reasonable agreement to the value of 7.3 measured under ambient conditions. At 107°C and 250 psi the model predicted a slightly lower pH of 5.9 (at 107°C, 250 psi), which may indicate that at ambient conditions re-equilibration of equations 1 – 3 above may result in a slightly higher pH than expected at elevated temperature and pressure. Moreover, if the predicted results are correct, then more extensive evolution of CO₂ may occur in the open system resulting in a higher "measured" pH prior to testing.

pH adjustment => 6.0 [Bicarb] = 500 ppm in brine/1 (250 ppm in mixed brine system). In the experiments reported above, it was required to reduce the pH of brine/1 to 2.08 prior to mixing in order to record a "mixed pH" of 6.0 following mixing of brine/1 and brine/2 under ambient conditions (20°C, atmospheric pressure). When modelling this system, a final (mixed) pH of 3.25 was predicted at 20°C and atmospheric pressure compared with a predicted pH of 3.5 under dynamic test conditions (107°C, 250 psi). The predicted low *in situ* pH of 3.5 would explain the recorded poor performance of the two commercial scale inhibitors observed experimentally under these conditions. Although a low pH is predicted by the model at ambient conditions, it must be remembered that the model system is constrained to a closed system, thus preventing loss of CO₂ to the surroundings. In a closed

system, evolution of CO₂ would be constrained by its partial pressure (as in the crimped vial static tests reported by other workers)³ resulting in a lower solution pH even under atmospheric conditions. In an open system, CO₂ evolution will occur, allowing the pH to rise.

Series (III) Low Sulphate and Carbonate Scaling Brine Systems

In this section is described a systematic investigation of the effects of several variables on the results of dynamic carbonate and sulphate tube blocking inhibitor performance tests in low scaling carbonate and low scaling sulphate brine systems. The variables investigated were:

- a) Flow rate
- b) Coil dimensions (coil length 1000mm and 3000mm)
- c) Run Time (pass criteria < 1 psi increase in DP over 60, 240 and 480 minutes of run time)
- d) Presence of prescale
- e) Effect of mixed scale (i.e. introduction of a very mild sulphate scale potential into the carbonate performance tests and *vice versa*)

Two brine systems were chosen for this investigation. An 80:20 mix of Brent FW/SW was chosen to represent a low barium sulphate scaling regime and a Milne Point FW was chosen to represent a low calcium carbonate scaling regime. In all tests, three generic scale inhibitor types were tested, the chemical structures of which are shown in Figure 1. These were

- a) DETPMP, a phosphonate
- b) PPCA, a polyphosphinocarboxylic acid, and
- c) PVS, a polysulphonic acid.

Low Barium Sulphate Scaling tests.

Effect of Flow rate. In these tests, an MIC was determined for each of the three generic scale inhibitors at three different flow rates, Q, of 3 mls/min, 10 mls/min and 20 mls/min (total flow rate brine /1 + brine/2). The results obtained are shown in Table 4a. It is evident that altering the flow rate has no impact on the recorded MIC, irrespective of the type of scale inhibitor being tested. However, increasing the flow rate can significantly reduce the time taken for scaling to occur. This can therefore allow initial screening tests to be conducted more rapidly by reducing the pass / fail criterion to > 2x blank scaling time prior to more detailed MIC determinations over longer run times as described below. In these tests, at 20 ml/min > 2 x the blank scaling time would equate to ~ 30 minutes at Q = 20 ml/min compared with 90 minutes at Q = 3 ml/min and therefore low flow rates may reduce the potential to pre-screen a large numbers of chemicals under realistic laboratory timescales.

Effect of Coil length. In these tests, an MIC was determined for each of the three generic scale inhibitors using coils of

length 1000 mm and 3000 mm. Tests were conducted at a flow rate of 20 ml/min. Increasing the coil length in this system had no impact on the recorded MIC, irrespective of the type of scale inhibitor being tested. In these tests a relatively insignificant reduction in the blank scaling time was recorded. However, in lower scaling environments including other mild sulphate scaling systems not directly examined in this paper, increases in the coil length and / or reducing the internal bore can significantly reduce the blank scaling time. As with the impact of flow rate described above, this can allow pre-screening of many more chemicals during initial product selection studies.

Effect of Run Time. In these tests, an MIC was determined for each of the three generic scale inhibitors over different time periods, namely 1 hour, 4 hours and 8 hours. The results obtained are summarised in Table 4b. No difference in MIC is observed for any of the three generic scale inhibitors on extending the test time from 1 hour to 8 hours.

Effect of Prescale. In these tests, the tube-blocking coil was prescaled to an increase in differential pressure of 1 psi prior to introduction of the scale inhibitor. Such a test provides a better mimic of field conditions, where there is likely to be some pre-existing scale growth present. The results obtained are summarised in Table 4c. No difference in performance was observed for DETPMP or PPCA in the presence of prescale. However, PVS showed a decrease in performance from an MIC of ~ 3.0 (MIC recorded in Table 4c as 3.0 - 5.0 ppm, fail time at 3 ppm of 230 minutes) to 5 - 10 ppm (fail time of 64 minutes at 5 ppm) when prescale was present. The indication from this work is that the PVS in this brine system is acting more efficiently as a nucleation inhibitor rather than a crystal growth blocker. Thus DETPMP and PPCA were effective at preventing crystal growth at their pass concentration recorded for non pre-scaled coils. The PVS, however, was not as effective at preventing crystal growth at its previously determined pass concentration in non-pre-scaled coils. The indication is therefore that the PVS is acting more effectively as a nucleation inhibitor or as a dispersant / anti conglomerant in delaying initial nucleation within the micro-bore coils.^{2,3} However, once initial scale formation has occurred it is less able to prevent further growth requiring a higher subsequent MIC. Note: this does not mean that the PVS does not function as a crystal growth inhibitor in this brine system, more that its relative effectiveness when compared to its efficacy at delaying initial nucleation is reduced and therefore an increased threshold level is required.

Effect of Mixed Scale. In these tests, a mild carbonate scaling potential was introduced by the addition of 250 ppm of bicarbonate ions into the mixed brine system. Initial examination of the PPCA involved adjustment and monitoring the "mixed brine" pH to 5.5 under ambient conditions in a similar manner to that described in series (I) above. In this test an increased MIC of 3 - 4 ppm was recorded as indicated

in Table 4d. As discussed above, this is thought to relate to a reduced test pH in the dynamic scaling coil. Further tests were therefore conducted with no adjustment of test pH. This resulted in a system pH under ambient conditions of 7.5, compared with 5.5 for the tests conducted in sets (a) - (e). In this final set of tests the performance of all inhibitor species was improved. However, as described previously, ineffective pH control would considerably influence both the recorded MIC values and the relative ranking of different inhibitor products. This is illustrated for the test involving PPCA at pH 5.5, in which it is thought that poor system pH control resulted in a reduced *in situ* pH within the test coil and a subsequent increase in recorded MIC.

Low Calcium Carbonate Scaling Tests

Effect of Flow rate. In these tests, an MIC was determined for each of the three generic scale inhibitors at three different flow rates. The results obtained are shown in Table 5a. It is evident that altering the flow rate has no impact on the recorded MIC, irrespective of the type of scale inhibitor being tested. However, increasing the flow rate can significantly reduce the time taken for scaling to occur and allow the performance test to be completed more rapidly as described for the low scaling sulphate system above.

Effect of Coil length. In these tests, an MIC was determined for each of the three generic scale inhibitors using coils of length 1000 mm and 3000 mm. Tests were conducted at a flow rate of 20 ml/min. As with the sulphate tests, increasing the coil length in this system had no impact on the recorded MIC. However a 50% reduction in blank scaling time was recorded. As with the impact of flow rate described above, this can allow pre-screening of many more chemicals during initial product selection studies.

Effect of Test Duration. In these tests, an MIC was determined for each of the three generic scale inhibitors over different time periods, namely 100 minutes, 4 hours and 8 hours. The results obtained are summarised in Table 5b. While the MIC of the phosphonate based product changed little over extended run times, the other two products (and in particular the PVS) showed a noticeable decrease in performance at longer test duration's. Thus in a low carbonate scaling environment, test duration is an important criterion when selecting inhibitors. Some scale inhibitors may delay crystal growth while others prevent such growth. Longer run times therefore allow these two effects to be distinguished.

Effect of Prescale. In these tests, the tube-blocking coil was prescaled to an increase in differential pressure of 1 psi prior to introduction of the scale inhibitor. Such a test provides a better mimic of field conditions, where there is likely to be some pre-existing scale growth present. The results obtained are summarised in Table 5c. In this brine system, PVS is less effective at preventing growth. This finding is consistent with the previous indications that while PVS may inhibit nucleation

or aid dispersion in this brine system, it is much less effective at preventing growth of carbonate scale on pre-existing carbonate surfaces.

Effect of Mixed Scale. In these tests, a mild barium sulphate scaling potential was introduced by the addition of 200 ppm of sulphate ions into the mixed brine system. Although a slightly shorter blank scaling time was observed, no significant difference in performance was recorded following inclusion of a low sulphate scaling potential in this brine system.

Summary of Results, Series (III)

Carbonate system. In summary, the low scaling carbonate system would appear to be much more susceptible to changes in test conditions than the low scaling sulphate system examined in this paper. Certain products, in particular the PVS, do not appear to completely prevent tube blocking although the rate of tube blocking is considerably reduced. This means that increasing the run time from 100 minutes to 8 hours produces a significant increase in MIC for such products. Other products such as DETPMP which appear more effective at completely stopping carbonate scale formation and growth in this brine system are therefore much less affected by increased run times. With this in mind the conclusion would be that long run times, or a reduced pass/fail criterion i.e. no increase in DP over 240 minutes would be recommended.

Pre-scale tests, Carbonate Scale. When examining pre-scale tests, it is evident that the problems relating to incomplete inhibition discussed above are exacerbated. In these tests the performance of PVS was considerably reduced. This may indicate that in this brine system the PVS inhibitor is acting more as a dispersant / anti agglomerant or by a nucleation inhibition pathway rather than a crystal growth inhibition. Thus extending run times and introduction of pre-scale coils significantly alters the ranking of different scale inhibitor products.

Recommended test protocol, low carbonate scaling regime. The recommended test protocol, representing a worst case test regime, would include pre-scale tests for low scaling carbonate brine systems. The recommended procedure would be to determine inhibitor performance following pre-scale with a 2 hour pass criterion of < 1.0 psi increase in differential pressure. In addition, any adjustment in the pH of the feed brines can lead to lower *in situ* pH values which may lead to inappropriate results. Thus great care is required if lower test pH's are required, this may require a combination of pH modelling and the use of *in situ* pH probes to record the actual brine pH following *in situ* mixing within the micro-bore coils.

Sulphate system. Unlike the carbonate system, the sulphate system appears much more robust to increases in test run time for the generically different products examined in this study. However it must be remembered that the three products

examined (PPCA, DETPMP and PVS) are known to be effective sulphate scale inhibitors. It is therefore not conclusive that extending run times would not result in poorer performance for less efficient sulphate scale inhibitors. In the pre-scale tests, the PVS recorded a higher MIC whereas the PPCA and DETPMP recorded identical MIC's to those recorded in the non-pre-scale tests. This indicates the greater ability of the PPCA and DETPMP to inhibit crystal growth in this brine system. At the fail concentration, tube blocking occurred much more rapidly, as may be expected.

Recommended test protocol, low sulphate scaling regime.

The recommended test protocol, which represents a worst case test regime, would be to include pre-scale tests for low scaling sulphate brine systems. Although this did not impact significantly on the performance results recorded in this work for the PPCA and DETPMP inhibitors it did impact on the performance of PVS. It would also be expected to show significant impact if less effective products were under examination. In addition, the presence of the pre-scale means that when inhibitor concentration drops below MIC, more rapid scaling occurs. The recommended procedure would be to determine inhibitor performance following pre-scale with a 2 hour pass criterion to < 1 psi increase in differential pressure.

Mixed scales. Inclusion of a mild sulphate scaling regime into a more severe carbonate scaling regime did not significantly impact inhibitor performance. However, inclusion of a mild carbonate scaling regime into a sulphate scaling brine does impact significantly on inhibitor performance. In a similar manner to that recorded in the experiments described in series (I) and Series (II) of this paper, it is indicated that poor pH monitoring and adjustment leads to a lower *in situ* test pH and consequentially poorer performance and potentially inappropriate chemical ranking. When tested with the pH unadjusted, improved performance was recorded. Thus, when examining downhole lower pH conditions, the inclusion of carbonate and subsequent poor pH adjustment and control can lead to significant errors in product ranking. It is therefore not recommended to include bicarbonate ions in tests examining sulphate scale under downhole (low pH) conditions. In addition, when examining carbonate scale, any adjustment in the pH of the feed brines can lead to lower *in situ* pH values which may again lead to inappropriate results. Thus for tests involving bicarbonate ions, great care is required if lower test pH's are required.

Conclusions

It is clear from this study that in order to obtain consistent results from different laboratories, the testing procedures used must be agreed upon and adhered to. The procedures must attempt to mimic field conditions as close as possible in order to derive both a true ranking and also determine appropriate MIC values. The consequences of selecting a less effective product and overestimating or underestimating a field MIC

level are more significant in today's complex subsea reservoir systems in which well access or re-treatment costs can be extremely expensive. Moreover, in complex subsea reservoirs, in which fluids from several production wells are often commingled at a subsea template and produced along single seabed flowlines, monitoring from individual wells remains an unsolved challenge.^{7,20} The extremely high costs associated with well access means that it is more important than ever to select appropriate inhibitor dose levels (MIC values) in the laboratory rather than rely upon subsequent optimisation in the field.

In this paper, we have demonstrated that seemingly small changes in test procedure can have a dramatic impact on the results obtained, altering the observed MIC for an inhibitor and, in some cases, even altering the performance ranking of a series of scale inhibitors. Carbonate scaling regimes appear to be more susceptible than barium sulphate scale to these effects, due in large part to the difficulty in achieving good *in situ* pH control in the presence of bicarbonate. The findings detailed in this paper can therefore be summarised thus:

- 1) Test conditions should be aligned across all testing laboratories if comparable results are to be obtained.
- 2) For a complete understanding of the inhibitor activity profile, both static and dynamic tests should be performed.
- 3) Bicarbonate ions should, if possible, be omitted from static barium sulphate inhibitor efficiency tests, as poor pH control will give unrealistic estimations of field behaviour.
- 4) When bicarbonate-containing brines are to be used in dynamic tests, pH must be effectively controlled.
- 5) For low scaling carbonate and sulphate systems, dynamic tests should be conducted with prescale and using a stringent pass/fail criterion (e.g. no increase in differential pressure over the test).

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Appendix A Test procedure for Mungo dynamic performance tests.

Brine Preparation. Two composite brines were prepared, in order to keep scaling cations (Brine 1) and scaling anions (Brine 2) separate, such that mixing them in a 50:50 ratio would give 50:50 Mungo Formation Water/Seawater. The freshly prepared brines were filtered through 0.45µm membrane filter. The two brines were then degassed under vacuum before use. After degassing the pH of brine/1 was adjusted as required and the bicarbonate (if required) added to brine /2 immediately prior to use

The test conditions used in this study were as follows:

System Pressure:	Initial MIC tests: 250 psi (17 bar)
System Temperature:	107°C
Coil dimensions:	ID ~0.8 mm L => 1,000 mm
Brine mixture:	50:50 Brine /1: Brine /2 to give 50:50 Mungo FW / SW. Brine compositions given below.
Blank run:	Ensure tube blocking ~ 30 minutes to > 1 psi increase in Differential Pressure.

Tube cleaning:	10% EDTA.
Pass/Fail criterion:	Initial tests (250 psi) 1psi increase in DP over 4 hour.
Flow rates:	6 ml /min combined flow rate (50:50 mix, 3ml/min per brine).
pH Adjustment:	As indicated in Table 1

Appendix B Recommended test procedure for low carbonate scaling regimes.

Brine Preparation. Two composite brines were prepared, in order to keep scaling cations (Brine 1) and scaling anions (Brine 2) separate, such that mixing them in a 50:50 ratio would give 100% Milne Point Formation Water. The freshly prepared brines were filtered through 0.45µm membrane filter. The two brines were then degassed under vacuum before use. After degassing the pH of brine/1 was adjusted as required and the bicarbonate ions were added to brine /2 immediately prior to use.

The test conditions used in this study were as follows:

System Pressure:	1500 psi (~100 bar)
System Temperature:	85°C
Coil dimensions:	ID ~ 0.8 mm L => 3,000 mm (and 1,000 mm)
Brine mixture:	100% Milne Point FW
[Bicarbonate]:	1900ppm in mix
Blank run:	Ensure tube blocking ~ 30 - 40 minutes at 10ml/min, > 2 psi increase in Differential Pressure
Tube cleaning:	10% acetic acid
Pass/Fail criterion:	> 1 psi increase in differential pressure over following run times: Set (a): 100 minutes Set (c): 240 minutes Set (d) 480 minutes Set (e) pre-scale 240 minutes Set (f) Mixed scale 60 minutes (Note: Blank scale < 30 minutes)
Pre-scale	Sets (a), (b), (c), (d) and (f) - No pre scale Set (e) pre-scale to 1 psi increase in DP prior to introduction of inhibitor.
Flow rates:	10 ml /min combined flow rate.
pH Adjustment:	pH brine 1 adjusted to 2.6, pH brine 2 not adjusted, recorded as pH = 7.7, Mixed pH ~ 7.5 (recorded at 20 C).

Appendix C Recommended test procedure for low sulphate scaling regimes.

Brine Preparation: Two composite brines were prepared, in order to keep scaling cations (Brine 1) and scaling anions (Brine 2) separate, such that mixing them in a 50:50 ratio would give 80:20 Brent Formation Water/ Seawater. The freshly prepared brines were filtered through 0.45µm membrane filter. The two brines were then degassed under vacuum before use. After degassing the pH of brine/1 was adjusted as required and the bicarbonate ions were added to brine /2 immediately prior to use.

The test conditions used in this study were as follows:

System Pressure:	1500 psi (~100 bar)
System Temperature:	85°C
Coil dimensions:	ID ~ 0.8 mm L => 3,000 mm
Brine mixture:	50:50 to give 80:20 Brent FW : SW
Blank run:	Ensure tube blocking ~ 30 minutes at 10ml/min, to > 2 psi increase in Differential Pressure
Tube cleaning:	10% EDTA
Pass/Fail criterion:	> 1 psi increase in differential pressure over following run times: Set (a): 100 minutes Set (c): 240 minutes Set (d) 480 minutes Set (e) pre-scale 240 minutes Set (f) Mixed scale 60 minutes (Note: Blank scale < 30 minutes) Sets (a), (b), (c), (d) and (f) - No pre scale Set (e) pre-scale to 1 psi increase in DP prior to introduction of inhibitor.
Flow rates:	10 ml /min combined flow rate.
pH Adjustment:	Sets (a), (b), (c), (d) and (e). Mixed pH 5.5

Set (f), mixed scale : pH brine 1 adjusted to 5.5, pH brine 2 not adjusted, recorded as pH = 5.5, Mixed pH ~ 5.5 (recorded at 20 C and 85 C).

Table 1: Brine Compositions used in this work

Ion	Mungo FW	Milne Point FW	Brent FW	Seawater
Na ⁺	23942	9800	9378	10890
Ca ²⁺	3914	175 ^a	286	428
Mg ²⁺	403	70	314	1386
K ⁺	1064	63	252	460
Ba ²⁺	120	25	80	0
Sr ²⁺	489	6	48	0
SO ₄ ²⁻	0	0 ^b (200)	592	2960
HCO ₃ ⁻	500	1900	0 ^c (250)	0

Notes: a) [Ca²⁺] increased to 175ppm to induce scaling
b) Sulphate only included for mixed-scale tests
c) Bicarbonate only included for mixed scale tests

Table 2: Test Conditions for Series (II) static barium sulphate efficiency tests

Test	pH	[HCO ₃] (ppm)
a	Buffered @ 6.0	0
b	Buffered @ 5.5	0
ci	Adjusted to 7.0	0
cii	Adjusted to 8.0	0
d	Adjusted to 6.0	250
e	> 7 (no adjustment)	250

Table 3: Mungo Series (II) static & dynamic test results

a) Static Barium Sulphate Efficiency Tests				
pH*	[HCO ₃] (ppm)	Pol M.I.C. (ppm)	Phos1 M.I.C. (ppm)	
5.5	0	10 - 15	4 - 5	
6.0	0	10 - 15	3 - 4	
7.0	0	10 - 15	3 - 4	
8.0	0	10 - 15	3 - 4	
6.0	250	10 - 15	3 - 4	
> 7	250	10 - 15	< 3	
b) Dynamic Carbonate Scale Performance Tests				
pH*	[HCO ₃] (ppm)	Pol M.I.C. (ppm)	Phos1 M.I.C. (ppm)	PVS M.I.C. (ppm)
2.5	0	> 200	> 100	1
6.0	0	5 - 10	2 - 5	1
5.5	250	> 60	> 60	-
6.0	250	> 40	20 - 40	-
> 7	250	5 - 10	2 - 5	-
c) Effect of System Pressure on dynamic carbonate scale performance tests				
System Pressure	Pol M.I.C. (ppm)	Phos1 M.I.C. (ppm)		
150 psi	20 - 25	20 - 25		
1000 psi	25	50		

*pH recorded for mixed brines under ambient conditions

NB: PVS MIC based upon active SI content, whereas Pol and Phos1

MIC's based on supplied concentrations.

Table 4: Series (II) Low Barium Sulphate Scaling Test Results

a) Effect of Flow Rate				
Flow Rate (ml/min)	Blank Scaling Time	DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
20	10 - 15 min	2.5 - 5.0	1.25 - 2.50	1.25 - 2.50
10	45 min	2.5 - 5.0	1.25 - 2.50	1.25 - 2.50
3	45 min	2.5 - 5.0	1.25 - 2.50	1.25 - 2.50
b) Effect of Test Duration				
Test Duration		DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
60 mins		2.5 - 5.0	2.0 - 3.0	3.0 - 5.0
240 mins		2.5 - 5.0	2.0 - 3.0	3.0 - 5.0
480 mins		2.5 - 5.0	2.0 - 3.0	3.0 - 5.0
c) Effect of Prescale				
Test Conditions		DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
No prescale		2.5 - 5.0	2.0 - 3.0	3.0 - 5.0
Prescale		2.5 - 5.0	2.0 - 3.0	5.0 - 10
d) Effect of Mixed Scale				
Test Conditions		DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
No bicarb., pH 5.5 ^a		2.5 - 5.0	2.0 - 3.0	3.0 - 5.0
250 ppm bicarb., pH 5.5 ^a		-	3.0 - 4.0	-
250 ppm bicarb., pH 7.5 ^b		1.0 - 2.0	1.0 - 2.5	2.0 - 3.0

Notes: a) Mix pH @ ambient T. P. pH of base 1 adjusted to 2.1

b) Mix pH @ ambient T. P. pH of base 1 unadjusted

Table 5: Series (III) Low Carbonate Scaling Test Results

a) Effect of Flow Rate				
Flow Rate (ml/min)	Blank Scaling Time	DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
20	20 min	0.25 - 0.50	< 0.25	0.50 - 1.25
10	50 min	0.25 - 0.50	< 0.25	0.50 - 1.25
3	no scale	-	-	-
b) Effect of Test Duration				
Test Duration		DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
100 mins		< 0.25	0.25 - 0.50	1.0 - 1.25
240 mins		0.25 - 0.50	0.25 - 0.50	1.25 - 2.0
480 mins		0.25 - 0.50	0.75 - 1.5	> 5
c) Effect of Prescale				
Test Conditions		DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
No prescale		0.25 - 0.50	0.25 - 0.50	1.25 - 2.00
Prescale		0.25 - 0.50	0.50 - 0.75	4 - 6
d) Effect of Mixed Scale				
Test Conditions		DETPMP M.I.C. (ppm)	PPCA M.I.C. (ppm)	PVS M.I.C. (ppm)
100 min pass, no SO ₄ ²⁻		< 0.25	0.25 - 0.50	1.0 - 1.25
60 min pass, 200 ppm SO ₄ ²⁻		0.25 - 0.50	0.25 - 0.50	1.0 - 1.25

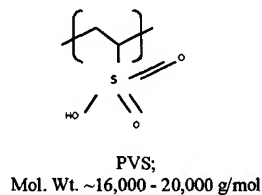
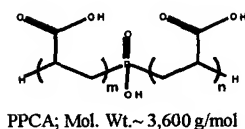
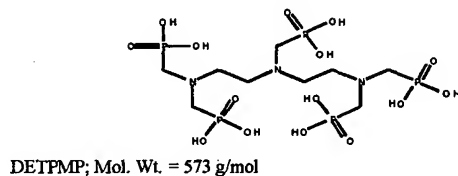


Figure 1: Molecular structures of the scale inhibitors DETPMP, PPCA and PVS

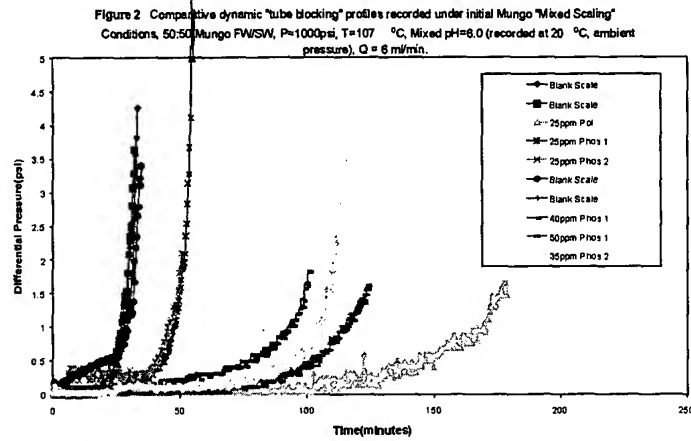


Figure 3: Comparative dynamic "tube blocking" profiles recorded under initial Mungo sulphate scaling conditions, 50:50 Mungo FW/SW, P = 250 psi, T = 107 °C, mixed pH = 8.0 (recorded at 20 °C, ambient pressure), Q = 6 ml/min

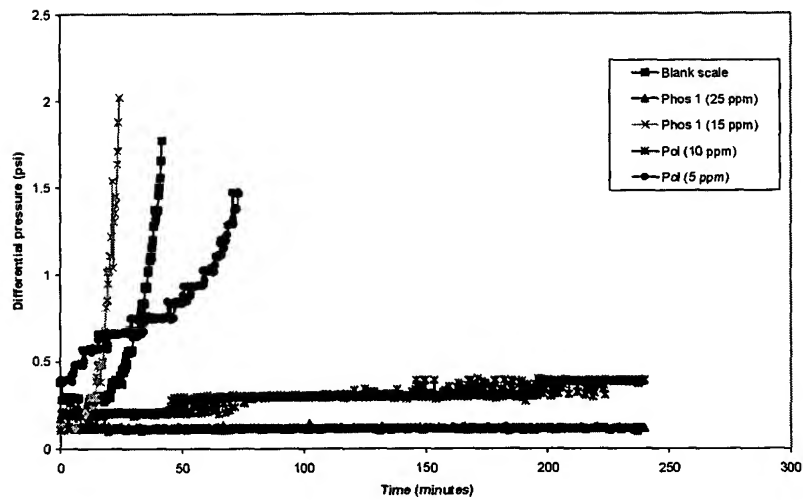


Figure 4: Static barium sulphate efficiency tests under Mungo test conditions for Polymer, $T=95^{\circ}\text{C}$
 $[\text{Pol}] = 10 \text{ ppm}$

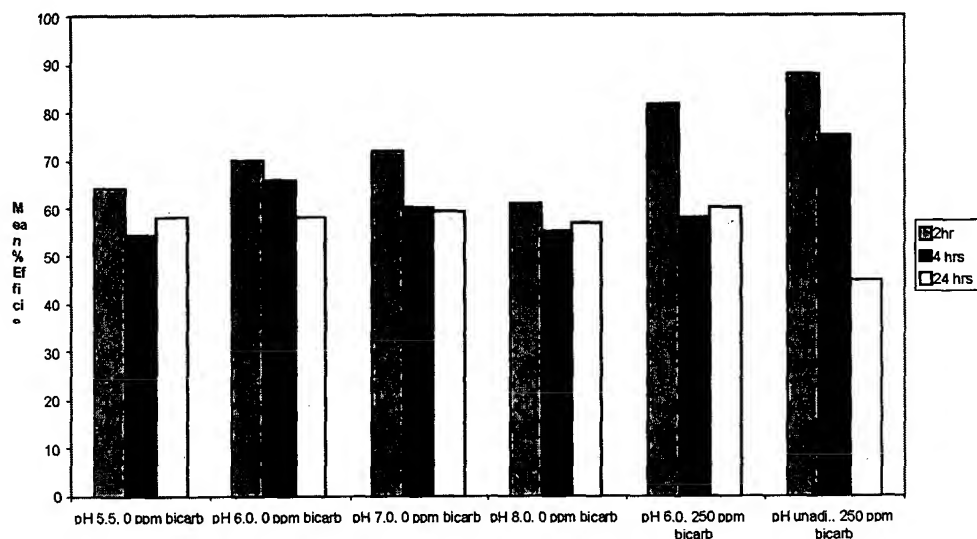


Figure 5: Static barium sulphate efficiency tests under Mungo test conditions for Phosphonate 1, $T=55^{\circ}\text{C}$, $[\text{Phos 1}] = 3 \text{ ppm}$

